EXTINGUISHMENT STUDIES OF HYDRAZINE AND UNSYMMETRICAL-DIMETHYLHYDRAZINE FIRES*

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I. INTRODUCTION

The employment of new high-performance liquid propellants has resulted in new problems of fire protection for personnel and facilities in the vicinity in which these chemicals are stored, handled, or used. By their very nature these propellants are reactive. Toxicity of the fuels or their combustion products may exist. Many of the fuel and oxidizer combinations are hypergolic, requiring no outside ignition source to start a fire. In other cases, these materials may burn as monopropellants without an outside oxidizer, making a particularly difficult extinguishment problem. The materials under discussion may be used in a wide variety of situations or geometries. This produces a wide variety of possible fire and explosion events. Yet, if these propellants are to be used, some form of fire protection must be provided.

This investigation was undertaken to determine the materials and techniques necessary for the extinguishment and control of fires involving two of these new propellants, hydrazine and unsymmetrical-dimethylhydrazine. Some properties of these fuels are shown:

Fuel	Formula	Boiling Point (°F)	Density (gms/cc)	Flash Point (closed cup) (°F)	Fire Point (°F)	Flammability Limits in Air Lower (vol per cent)	Flammability Limits in Air Upper (vol per cent)
Hydrazine	N_2H_4	236	1.008	104	126	4.7	100
UDMH	$(CH_3)_2N_2H_2$	146	0.786	34 (?)	5	2.5	95

The program also included studies of the 50-50 mixture of these fuels, the fuel JP-X (a solution of UDMH in JP-4, a petroleum fuel), and fires involving all these fuels in contact with nitrogen tetroxide in either liquid or vapor form. This paper is limited to a summary of data for the hydrazine or UDMH and air combinations. Further details including results from the other combinations, are available from the progress reports (1).

While the primary objective of the investigation was to determine the requirements for fire protection systems capable of coping with fires involving these propellants, an important by-product was the development of basic knowledge in the use of small models for fire-extinguishment research. Since the application of the results of this investigation to fire-extinguishment practice depends, in part,

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upon being able to extrapolate laboratory results to very large fires, the appropriate scaling factors must be well known. This involves determination of the mechanisms by which various agents extinguish fires and the effects of agent-application parameters, fire geometries, and fire size on the extinguishing capabilities of the various agents.

The experimental approach involved three fire sizes. The smallest test, 6.54-sq in, were conducted in a laboratory hood; providing an extensive amount of data to screen candidate agents, determine the mechanisms of extinguishment, and the optimum methods and rates of application. The burner shown in Figure 1, was a square stainless-steel pan which could be heated to maintain the fuel at a temperature above its fire point. A 3/4-inch freeboard on the sides of the pan reduced splashing and fuel spillage. Any propellant spillage or excess extinguishing agent was caught in the stainless steel tray on the sides of the pan. This tray also served to reduce the updraft caused by the fire and to prevent these updrafts from cooling the sides of the burner.

To evaluate an extinguishing agent, 0.6 to 2.4 cubic inches of fuel (corresponding to about 0.1 to 0.4 inches depth) were placed in the burner, allowed to reach the desired temperature, and ignited by means of a hot wire. After a selected preburn time, usually 10 seconds, the agent was directed onto the fire. The length of time required for extinguishment, the amount of agent required, and the amount of propellant remaining unburned were determined as a function of agent, rate of application, application technique, and propellant.

The larger pans, 49- and 324-sq in, were identical in geometry to the smallest pans and were used to determine the scaling factors necessary for extrapolation of the results to still larger fires. They were located in the outdoor facility shown in Figure 2. After the photograph was taken, an eight-foot-high windbreak was built around the facility to minimize the effects of variable winds.

In spite of all precautions, a substantial variability in the results of consecutive tests was found. This seems to be characteristic of pan fire extinguishment tests. Hence a large number of tests were made, and averages of a series of identical tests were used to compute each datum point plotted on the curves which follow. A total of 994 test fires were burned to obtain the results discussed herein.

II. EXPERIMENTAL RESULTS

A. BURNING RATES OF HYDRAZINE AND UDMH

Burning rates of hydrazine and UDMH were found from burning time vs. fuel depth curves for a series of square pans:

Fuel	Pan Area (sq in)	6.54	49	324
Hydrazine		0.74 in/min	0.47 in/min	1.41 in/min
UDMH		0.088 in/min	0.046 in/min	0.195 in/min

Hydrazine is seen to burn an order of magnitude faster than UDMH. This is ascribed to the ability of hydrazine to burn like a monopropellant; a decomposition flame not requiring oxygen exists close to the liquid surface. The hydrogen produced by this flame then burns with air as a diffusion flame. Addition of water to the hydrazine reduces its burning rate substantially.

The slower-burning UDMH has a burning rate of the same magnitude as ethanol or gasoline, so a decomposition flame is evidently not present.

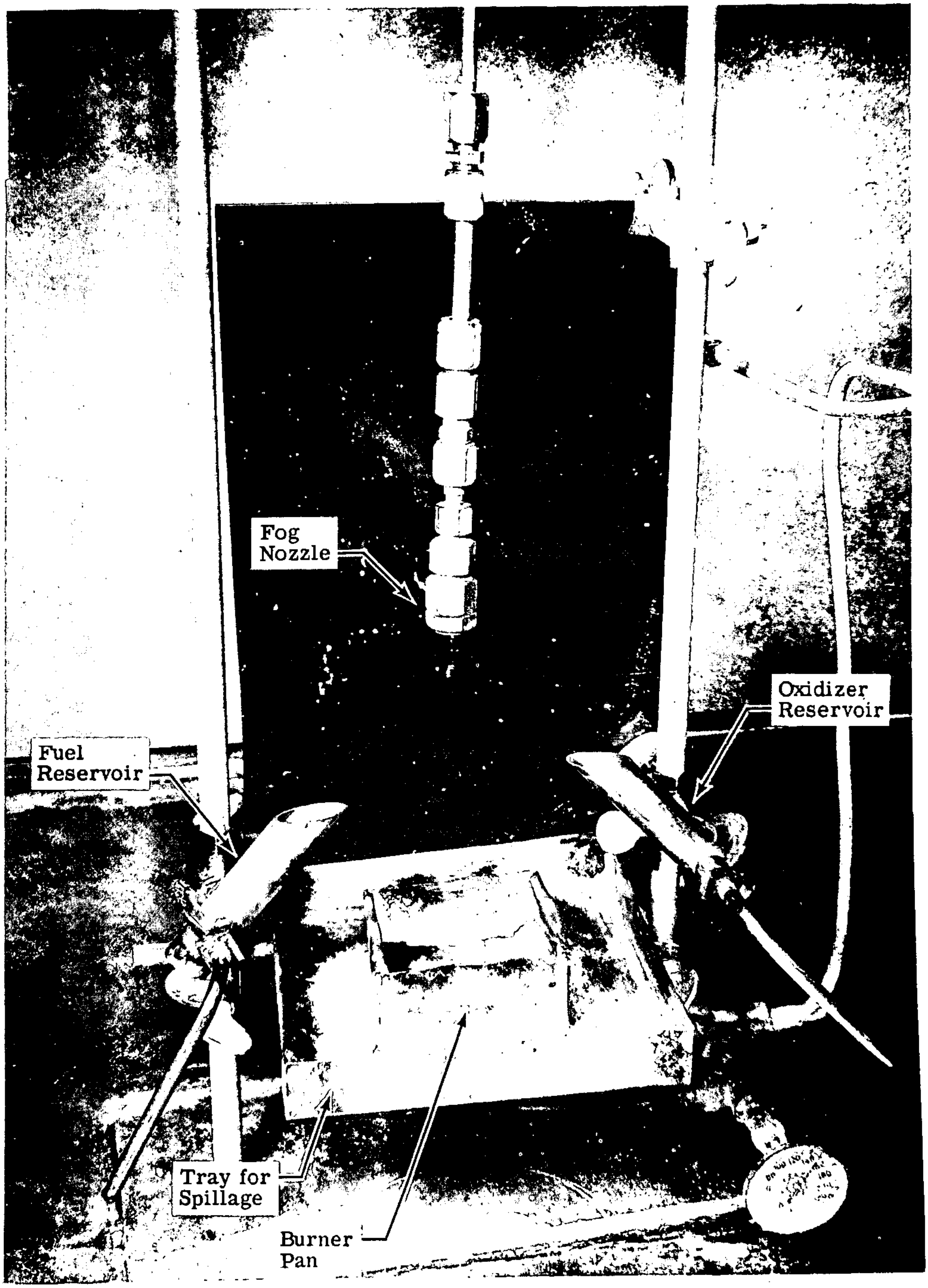

Figure 1. Burner Apparatus with Spray Nozzle.

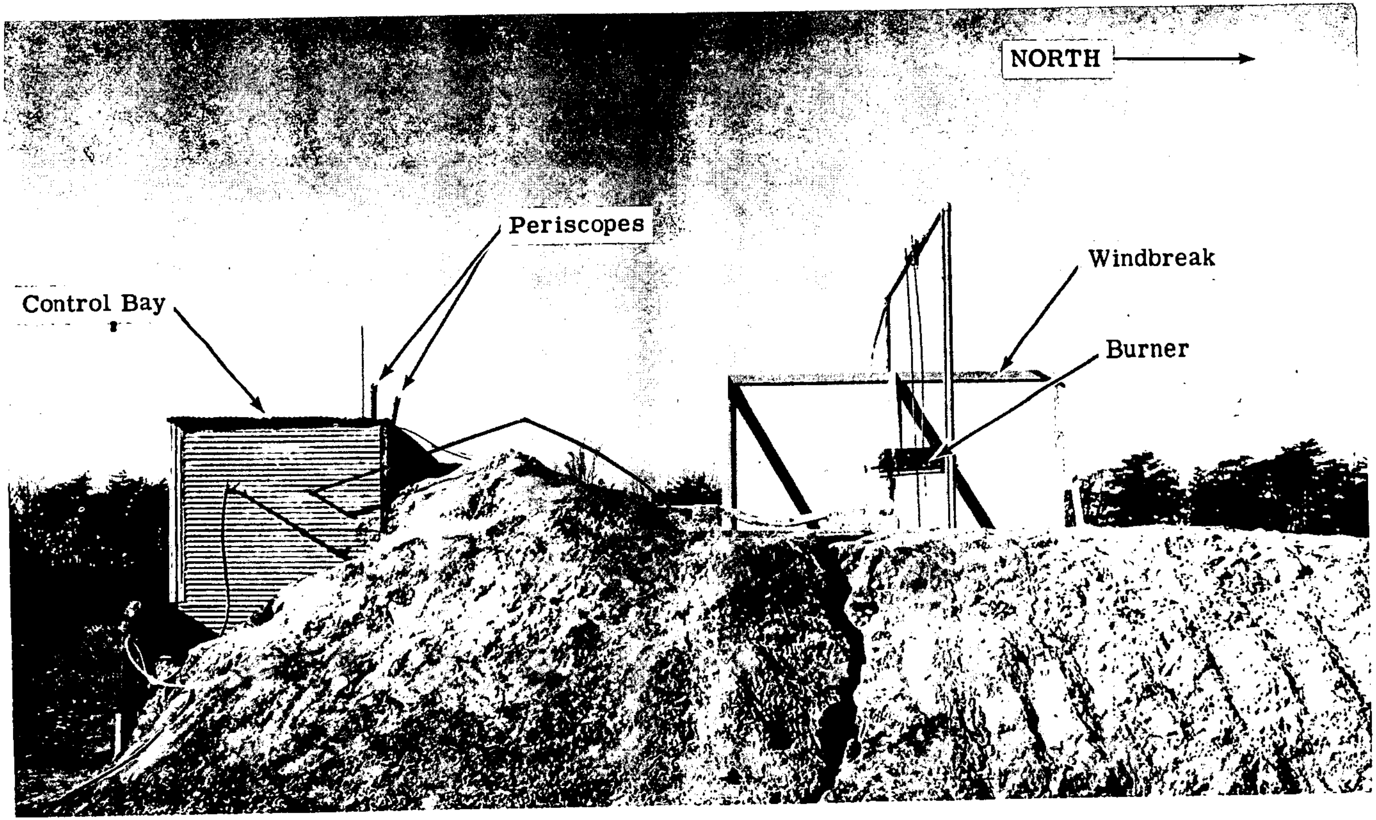

Figure 2. Side View of Outdoor Fire Extinguishment Facilities.

The variation with pan size for both fuels is explicable on a heat-transfer basis (2,3) and will not be discussed here.

B. EXTINGUISHMENT OF HYDRAZINE FIRES

1. Water Sprays

The mechanism by which water sprays extinguish hydrazine fires appears to be dilution of the hydrazine to a concentration which will not support combustion. As shown in Figure 3, when water was applied to 6.5-, 49-, and 324-sq in hydrazine fires at rates of 0.01 to 0.33 gal water/sec gal of fuel (0.2 to 1.2 gpm/ft^2), the hydrazine concentration after extinguishment indicated a dilution to 40-70 weight per cent. The residue remaining after extinguishment of the larger fires was more dilute than those from the smaller fires. In the larger fires, more heat was radiated to the liquid and therefore the liquid temperature was higher. This meant that more dilute solutions supported combustion. The concentration of hydrazine in the residue remaining after extinguishment was found to decrease as the depth of the fuel was decreased. Decreasing depth is indicated by increasing normalized water spray rate in Figure 3. Since water and hydrazine have approximately the same densities concentration gradients are easily established. Mixing depends mostly on the force with which the water spray impinges on the surface and the depth of the pool. Both effects are responsible for the decrease in the concentration of hydrazine in the residue as the normalized spray rate was increased as shown in Figure 3.

Since the mechanism of extinguishment is primarily one of dilution, in an idealized case the time that spray must be applied to cause extinguishment should be directly proportional to the amount of fuel present and inversely proportional to the rate of application of spray. However, the simplicity of the dilution mechanism is complicated by the following factors:

1) As the fire progresses, some of the fuel is consumed, leaving only the remainder to be diluted.
2) Some of the water which does reach the burning liquid is later vaporized.
3) Some of the water is vaporized in the flame and never reaches the burning liquid.
4) Mixing rate of the water and fuel is not instantaneous.

Because of the above factors, the length of time that spray must be applied is not simply proportional to the volume of fuel or the inverse spray rate. However, as shown in Figure 4, the data may be correlated by plotting the logarithm of the extinguishment time versus the logarithm of a normalized rate of application of spray (gal water/sec gal of fuel). In view of the above complicating factors, the fact that even an empirical correlation can be obtained is indeed fortuitous. The slopes and intercepts of the curves would be expected to be complex functions of the properties of the fuel, pan size, and agent. The main conclusion from the curves is that larger fires require a longer application of spray before extinguishment occurs, for the same normalized spray rate, but that the increased time is slight when compared to the increased fire size.

The percentage of original fuel remaining after extinguishment, an expression of the efficiency, is presented in Figure 5 as a function of the rate of application of water. As can be seen, faster rates of application are more efficient on this basis than slower ones, and deeper pools of fuel are more efficiently extinguished than shallow ones.

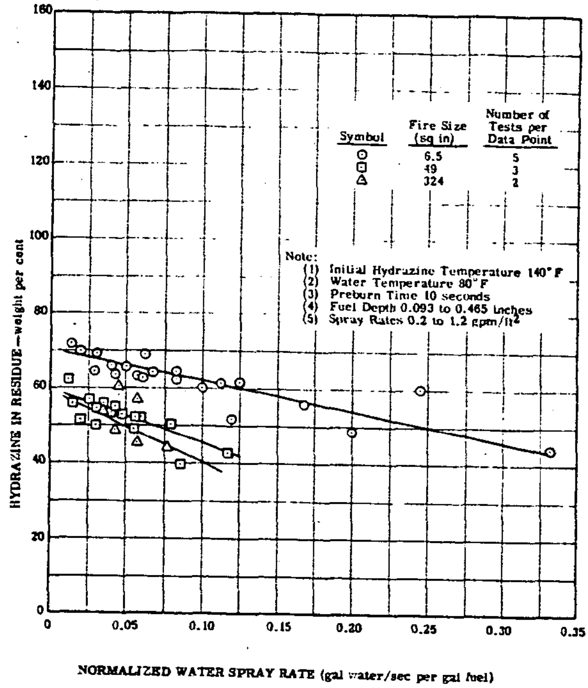

Figure 3. Concentration of Hydrazine in Residue Remaining after Extinguishment of Hydrazine Fires by Water Spray.

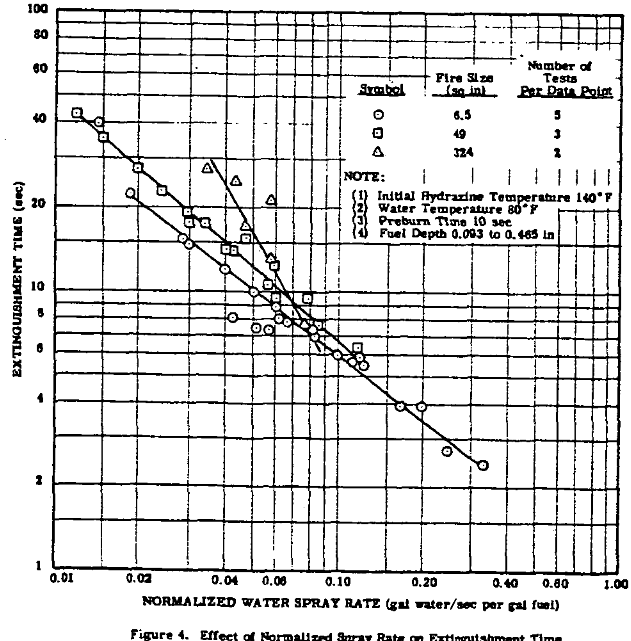

Figure 4. Effect of Normalized Spray Rate on Extinguishment Time of Hydrazine Fires.

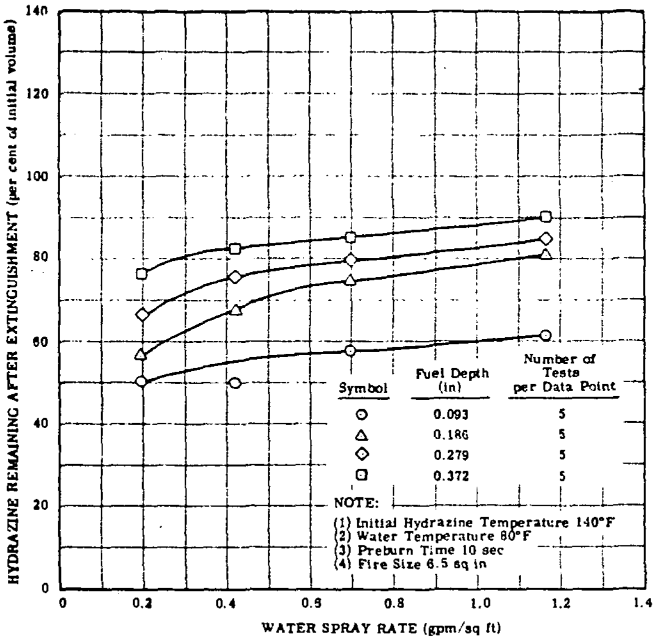

Figure 5. Effect of Water Spray Rate on Amount of Hydrazine Remaining after Extinguishment.

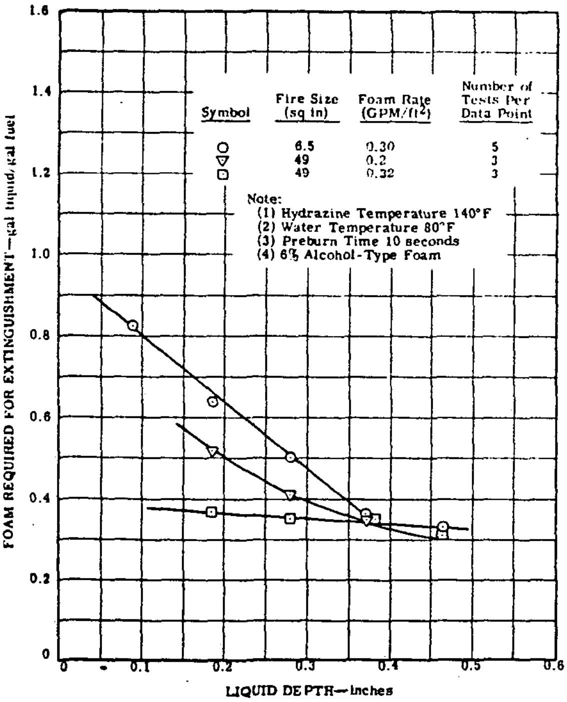

Figure 6. Effect of Liquid Depth on Amount of Foam Required for Extinguishment of Hydrazine Fires.

Because dilution is the mechanism by which water sprays extinguish hydrazine fires, the major scaling factor for extinguishment is a function of the amount of fuel present and is not a function of diameter, per se. However, spray rate, liquid depth, and fire diameter do influence scale-up slightly. Since dilution to 50 weight per cent concentration appears to be adequate, the amount of water required for extinguishment would be about one gallon per gallon of fuel. Any consumption of fuel or vertical concentration gradients would reduce the amount required. Conversely, any vaporization of water in the flame would increase the amount of water required.

The weight average particle size, $\bar{D}_w$, of the spray used on each fire size was:

Pan Size sq in	$\bar{D}_w$ microns
6.5	160
49	245
324	290

2. Fog

Measurements with the 6.5-sq in burner indicated that water fog was less effective than coarse water sprays against hydrazine fires. Since the concentrations remaining after extinguishment were comparable, the lower efficiency was probably due to increased vaporization of the fine droplets in the flame. Fog was less effective against 49-sq in fires than against 6.5-sq in fires, again because of vaporization in the flame, preventing liquid dilution. The fact that as much as 1.5 gallons of water per gallon of fuel originally present were required for extinguishment, in comparison to 1.0 gal/gal for spray, indicates the magnitude of the vaporization, especially since most of the fuel originally present was consumed in the fire.

Fog is not a good extinguishing agent for hydrazine fires and would probably fail to extinguish very large fires.

3. Foam

The mechanism by which foam* extinguishes hydrazine fires appears to be dilution of the surface of the burning liquid below the concentration which supports combustion. Since the hydrazine causes the foam to break down rapidly, a surface layer of water is built up over the fuel. The foam on top of the water film is stable until it contacts fresh hydrazine further out on the burning pool. When the foam blankets the entire surface, the fire is extinguished.

As shown in Figure 6, the amount of foam required for extinguishment is a function of application rate, depth of liquid fuel, and size of the fire. Faster rates of application require less foam because the foam has less time to break down and is therefore able to blanket the fire more quickly. Figure 7 shows that times required to extinguish the 49-sq in fires were about 10 seconds longer with 0.2 gpm/ft^2 application than with 0.32 gpm/ft^2. The slower rate of travel across the hydrazine surface at the lower application rate permits more breakdown of the foam, and therefore more foam is required.

The decrease in the amount of foam required per gallon of fuel for deeper pools of hydrazine confirms the mechanism of surface dilution. Although the concentrations of hydrazine remaining after extinguishment shown in Figure 8 are decreased by the

* A 6% alcohol-type foam was used at a 10 to 1 expansion ratio.

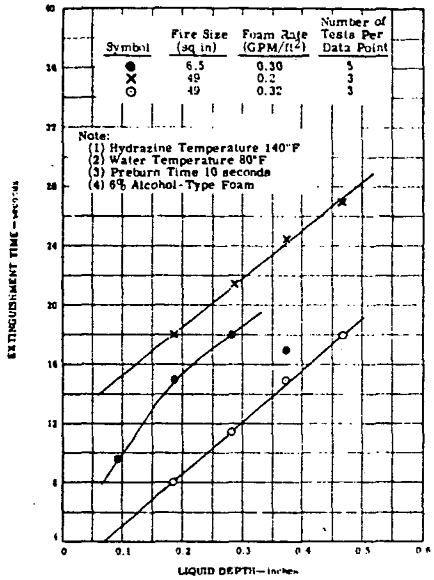

Figure 7. Effect of Liquid Depth on Time Required for Extinguishment of Hydrazine Fires by Foam.

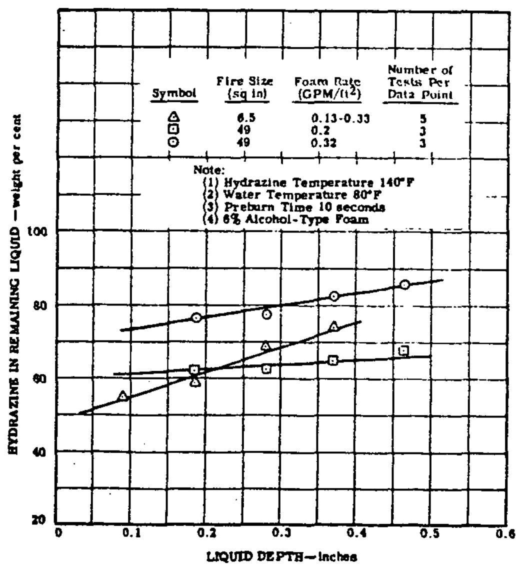

Figure 8: Effect of Liquid Depth on Concentration of Hydrazine Remaining after Extinguishment of Hydrazine Fires by Foam.

collapse of the foam blanket remaining after extinguishment, the fact that the final hydrazine concentration may be as high as 86 weight per cent shows that the concentration gradients are very steep.

The mechanism of surface dilution suggests that scaling factors are strongly dependent on surface area of the fire as well as liquid depth and stability of the foam. Any agitation of the fuel would disturb the concentration gradients and render the foam less effective. The foam should be distributed evenly over the surface and applied at as fast a rate as possible. Although foam is a more efficient extinguishing agent than water spray, the ease of application of water sprays and the required dilution below the fire point, which eliminates the reignition hazard, make water sprays more attractive than foam.

4. Dry Chemical

A modified sodium bicarbonate powder of 50 micron average particle size was very effective in extinguishing fires involving hydrazine and air. As seen in Figure 9, when as little as 0.016 $lbs/sec/ft^2$ was applied, the fires were extinguished in less than four seconds. The depth of burning liquid had no observable effect, but complete coverage of the burning surface was required before extinguishment occurred. This requirement is probably the cause of the apparently anomalous results in which more time was required for extinguishment at the faster rate. These results are similar to those obtained in the 6.5- and 324-sq in burners, in which 0.016 $lbs/sec/ft^2$ extinguished the fires in less than three seconds. After extinguishment the fires could be reignited by the hot wire igniter. In practice, therefore, some other agent such as water might have to be applied in addition to the dry chemical to prevent reignition after extinguishment had been achieved.

A solution of 8 per cent by weight sodium bicarbonate in water applied as a water spray at a rate of 0.6 gpm/ft^2 showed no improvement over water as an extinguishing agent in the 6.5-sq in burner. This is consistent with other work which has shown that extinguishment by dry chemical involves reactions in the flame.

A potassium bicarbonate powder of 25 micron diameter was as effective as the sodium bicarbonate. However, an ABC Type powder was ineffective against the hydrazine fires.

Scale-up in dry chemical extinguishment is a function of fire area. Good results with this agent are dependent on the ability of the extinguishing system to completely blanket the fire and thereby prevent flashover from reigniting the extinguished areas. Dry chemicals are attractive in that they can extinguish the fires in a comparatively short time with the minimum weight of agent.

5. Chlorobromomethane

Chlorobromomethane (CB) was sprayed on hydrazine fires at a rate of 0.11 gpm/ft^2 through the nozzles also used for water spray. The CB reacted with the hydrazine, increasing the intensity of the fire and producing dense white fumes. The fires continued to burn until the hydrazine was consumed. CB is ineffective as an extinguishing agent for hydrazine fires under these conditions.

6. Investigation of Other Agents

Several screening tests were made to determine if chemicals other than sodium bicarbonate could inhibit the combustion of hydrazine-type fuels. Since aniline is capable of trapping the $NH_2\cdot$ radical believed to be involved in the combustion process, this chemical was the first to be investigated. When 2 weight per cent aniline was added to hydrazine, the burning rate of the hydrazine was reduced by only 10 per cent. Since the alkali metal bicarbonates in powder form were so

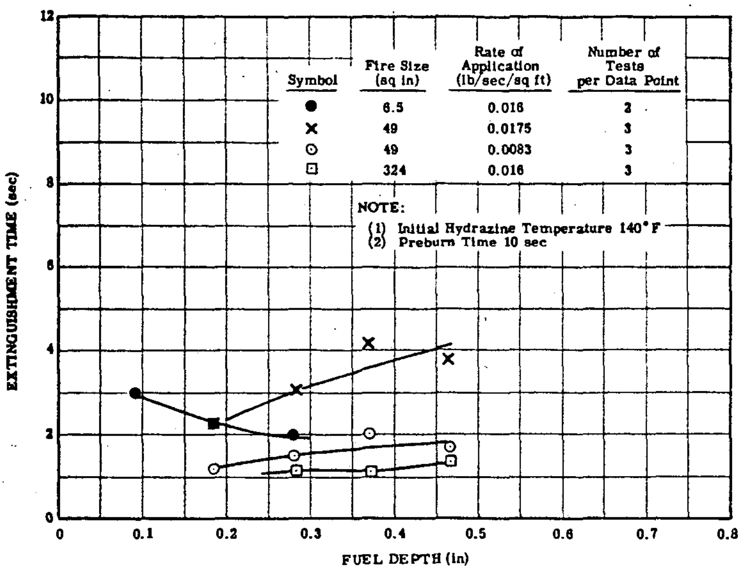

Figure 9. Effect of Fuel Depth on Extinguishment Time of Hydrazine Fires by Sodium Bicarbonate.

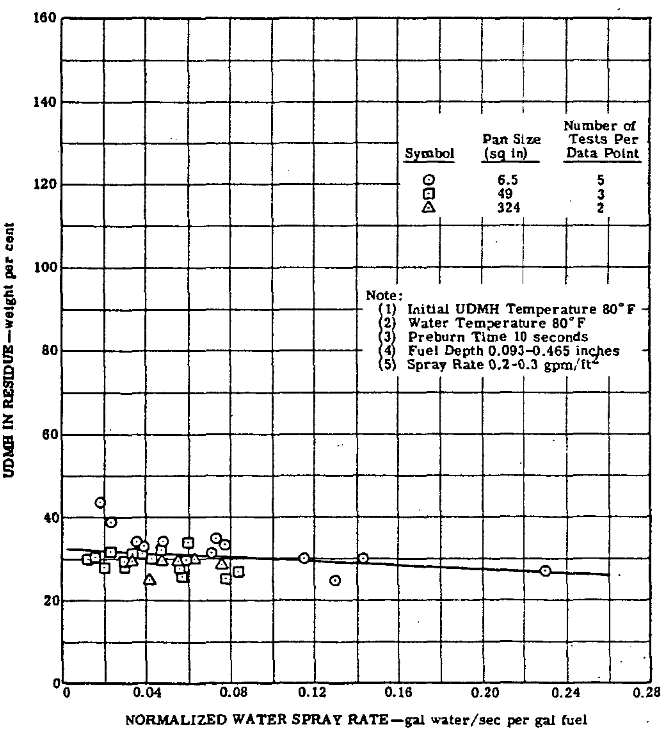

Figure 10. Concentration of UDMH in Residue Remaining After Extinguishment of UDMH Fires by Water Sprays.

effective against hydrazine fires, other methods of applying alkali metal salts were investigated. A solution containing 8 per cent by weight sodium bicarbonate showed no improvement over a plain water spray. Since potassium iodide is very soluble in hydrazine, a solution containing 20 grams of potassium iodide per 100 grams of hydrazine was burned. The combustion was slowed down considerably by the formation of a molten slag over the burning liquid, but all of the hydrazine was consumed. Addition of 10 weight per cent boric acid, (a constituent in some ABC powders) had a similar effect. It was thought that an inert liquid might blanket the surface of burning hydrazine and prevent combustion. However, a silicone oil added to burning hydrazine formed a film on the surface, but did not extinguish the flame.

C. EXTINGUISHMENT OF UDMH FIRES

1. Water Sprays

As was the case with hydrazine fires, the length of time that water sprays must be applied before extinguishment of UDMH fires occurs is a function of the amount of fuel present and the rate of application of the spray. This indicates that the mechanism of extinguishment of UDMH fires is also one of dilution of the burning liquid to a concentration which will not support combustion. The UDMH fires required a longer application of spray than did the hydrazine fires because more dilute solutions of UDMH will support combustion and the UDMH burns at a slower rate, thus consuming fuel more slowly. Figure 10 shows that the fires in the 6.5-, 49- and 324-sq in burners were extinguished when the UDMH concentration was reduced to approximately 30 weight per cent. This final concentration was the same for all spray rates, pan diameters, and liquid depths. Since water is more dense than UDMH, it is believed that good mixing occurred as the water settled through the UDMH.

As was the case with the hydrazine fires, the larger fires required a longer application of spray before they were extinguished, cf. Figure 11. Since the concentrations of UDMH remaining in the residue after extinguishment were comparable regardless of fire size, increased vaporization of the water droplets in the larger flames would appear to be the cause of the increased amount of water required for extinguishment.

The percentage of UDMH remaining after extinguishment as a function of spray rate is presented in Figure 12. As can be seen, faster spray rates are more effective for extinguishing UDMH fires than slower rates. There is little or no change in the percentage of fuel remaining after extinguishment as the depth of UDMH is increased. This indicates that a basic difference in extinguishment behavior arises from the more complete and rapid mixing of water with UDMH than with hydrazine.

2. Fog

Fog extinguished UDMH fires by the same mechanism as water sprays, i.e., dilution. Fog applied at a rate of 0.2 gpm/ft^2 against the 49-sq in fires required 2.13 gal/gal of UDMH as compared to 1.46 gal/gal of UDMH for water spray at the same rate. Fog does not seem as desirable as water spray against UDMH fires, since part of the fog evaporates and is unable to dilute the fuel.

3. Foam

Although UDMH caused the alcohol-type foam to break down, it nevertheless extinguished UDMH fires. As with hydrazine, the mechanism of extinguishment appears to be one of floating water on top of the burning liquid and diluting the surface below the concentration which will support combustion. Because this is a gentle application of water, concentration gradients are set up and the average concentrations of 35-55 weight per cent are well above the minimum concentrations which support combustion. Figure 13 illustrates this. As seen from Figure 14, the relative amount of liquid required for extinguishment decreases as the fuel depth is increased because

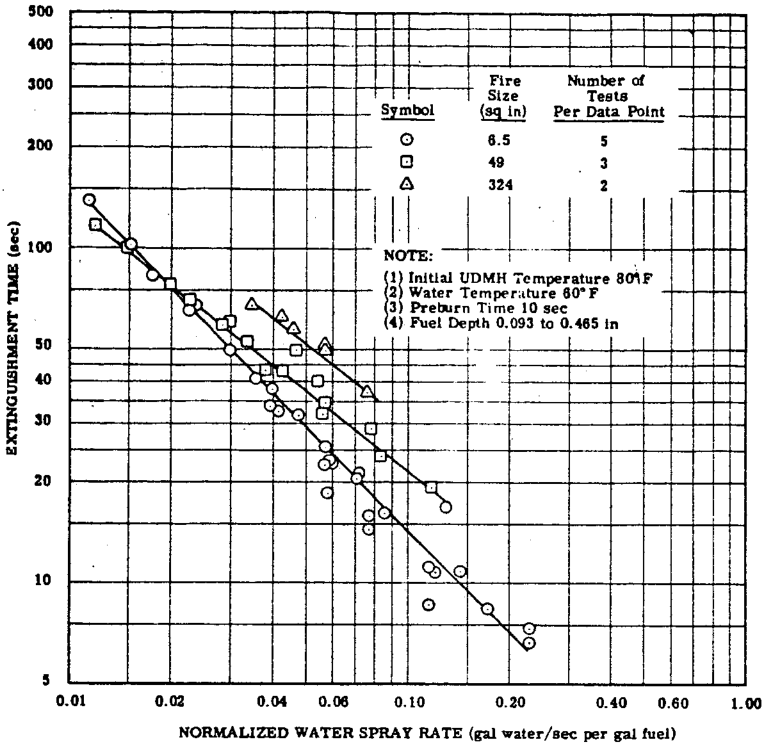

Figure 11. Effect of Normalized Water Spray Rate on Extinguishment Time of UDMH Fires.

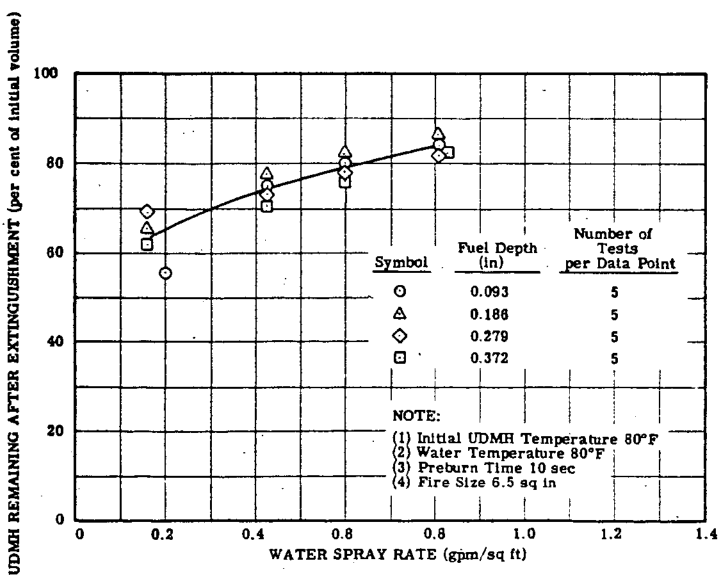

Figure 12. Effect of Water Spray Rate on Amount of UDMH Remaining after Extinguishment.

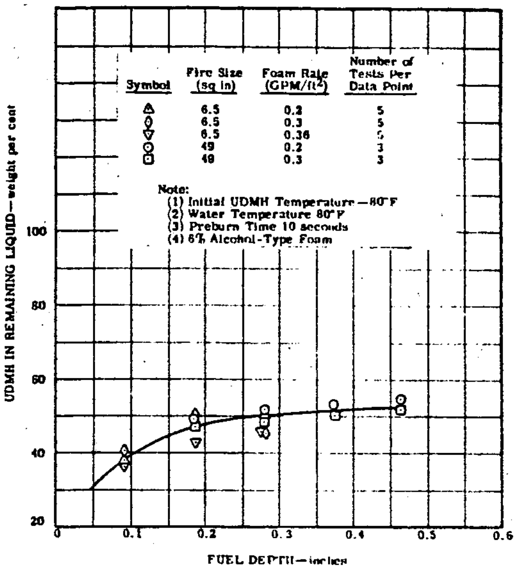

Figure 13. Effect of Fuel Depth on Concentration of UDMH Remaining after Extinguishment by Foam.

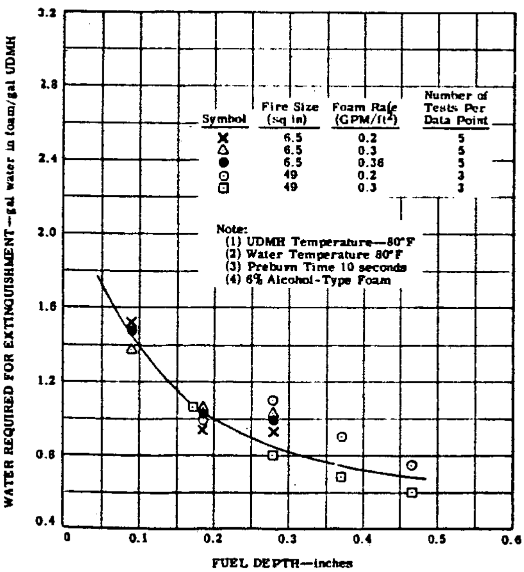

Figure 14. Effect of Fuel Depth on Amount of Liquid Required for Extinguishment of UDMH Fires by Foam.

of the concentration gradients mentioned above. The effectiveness of foam is increased by faster application rates. Increasing the pan diameter did not increase the amount of foam required per gallon of fuel at any given depth. The scaling factor would therefore be a function of volume of fuel, depth of fuel, and application rate.

As was the case with hydrazine fires, foam is a more efficient method of applying water to UDMH fires than is spray. However, if an adequate supply of water is available, the ease of application and the faster rates at which it can be applied make water spray more attractive.

4. Dry Chemical

Sodium bicarbonate powder rapidly extinguished UDMH fires. When the dry chemical was applied at rates of 0.0175 or 0.0083 lb/sec/ft^2 and when complete coverage of the surface was obtained, all fires were extinguished in less than 5.2 seconds. Fire size was varied from 6.5- to 324-sq in and depth of fuel from 0.093 to 0.47 inch. If complete coverage was not obtained, the fire flashed over the surface when the flow of agent was stopped. As was the case with hydrazine, the fire could be reignited by a hot wire. Dry chemical is particularly suitable when speed of extinguishment is important or when a minimum amount of agent must be applied.

5. Vaporizable Liquid Agents

As shown below, trichlorotrifluoroethane extinguished 6.54-sq in UDMH fires when applied at a rate of 0.5 gpm/ft^2. The fires could be reignited after extinguishment, but burned less intensely. Since trichlorotrifluoroethane has a boiling point of 115.7°F, and the fire point of UDMH is 34°F, cooling of the UDMH does not appear to be a mechanism of extinguishment. Although dense white fumes were given off when the trichlorotrifluoroethane contacted the burning UDMH, there was no increased intensity of the fire such as occurred when chlorobromomethane was added to hydrazine. Trichlorotrifluoroethane might be useful in locations where limited access to the fire is available. It appears to be somewhat more effective than water spray or foam.

Extinguishment of UDMH Fires by Trichlorotrifluoroethane:

Liquid Depth (inches)	Extinguishment Time (seconds)	Gallons of Agent per Gallon of UDMH
0.093	6.9	0.99
0.186	6.7	0.48
0.279	9.5	0.45
0.372	24.0	0.86

Notes:

1. Application rate: 0.5 gpm/ft^2
2. UDMH temperature: 80°F
3. Preburn time: 10 seconds
4. Fire Size: 6.5 sq in

D. EXTINGUISHMENT OF FIRES INVOLVING A MIXTURE OF HYDRAZINE AND UDMH

Although an investigation of fires involving a mixture of 50 parts each by weight hydrazine and UDMH is incomplete, enough data have been obtained to indicate that this mixture behaves very much like pure UDMH in regard to burning rate and quantity of agents required for extinguishment. The reason is that the vapor pressure of UDMH is much greater than that of hydrazine, so that the vapors above the mixture are essentially UDMH.

In addition to the agents applied to UDMH fires, several other agents have been tested against small fires involving the mixture. These agents were bromotrifluoromethane and carbon dioxide.

Bromotrifluoromethane, when applied at a rate of 0.04 lb/sec/ft^2 (0.18 gpm/ft^2), failed to extinguish fires involving the 50-50 mixture in the 6.54-sq in burner. The agent was applied in gaseous form and directed on the fire both from above and from the side. It did not react with the burning fuel. Further tests are in progress, with other methods of application.

Carbon dioxide when applied at a rate of 0.17 lb/sec/ft^2 failed to extinguish fires involving the 50-50 mixture in the 6.54-sq in burner. The carbon dioxide was applied in the gaseous form and no attempt was made to direct "CO_2 snow" on the fire.

III. CONCLUSIONS

Based on results to date the following conclusions are drawn:

1. Hydrazine fires can be extinguished by water sprays, alcohol-type foams, or dry chemical powders containing primarily sodium bicarbonate. Water sprays are best suited for spill-type fires. At least one gallon of water per gallon of fuel must reach the surface of the burning liquid. Foams can be used for deep pools or in chases where the water supply is limited. Dry chemicals should be used in cases where rapid extinguishment is necessary or when the amount of agent available is limited, and where reignition is not a problem. Chlorobromomethane should not be used against hydrazine fires.

2. UDMH fires may be extinguished by water sprays, alcohol-type foams, dry chemical powders containing primarily sodium bicarbonate, or trichlorotrifluoroethane. Water sprays are best suited for spill-type or deep-pool fires. Dry chemicals are effective when rapid extinguishment is necessary or when the supply of agent is limited, and reignition is not a problem.

3. Fires involving the 50-50 mixture of hydrazine and UDMH behave essentially as UDMH fires. The same quantities of agents are required for fires involving the mixture as for fires consisting of pure UDMH. Neither bromotrifluoromethane nor carbon dioxide have extinguished fires involving the 50-50 mixture, in testa to date.

IV. ACKNOWLEDGEMENTS

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